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ABSTRACT

PURPOSE: To obtain polyester particles having a low specific gravity, a low dielectric constant, closed holes inside, and specified particle size, void content, etc., by converting a polyester resin having ionic groups into perforated particles by a specific method.

CONSTITUTION: The title particles mainly comprise a polyester resin containing 20-200eq/ton ionic group and have a volume-average particle size of 0.5-100μm and a void content of 1-99vol.%, each particle containing one or more closed holes/cells filled with a gas or liquid. The particles are manufacture by dissolving the resin in a water-soluble organic compound. (e.g. ethanol) and adding water to the resulting solution to form a W/O/W emulsion, and are suitable as a delusterant, an antiblocking agent, a carrier for chromatography and the like.

What is claimed is

1. Polyester particle comprising: as a principal component, polyester resin containing 20-2000eq./ton of ionic groups and having volume average particle size D of 0.5-100μm, wherein the particle comprises one or more independent holes inside thereof filled with gas or liquid and the void ratio is 1-99 vol%.

[0001]

[Industrial Applicability]

This invention relates to perforated polyester resin particles which have many holes inside the particle. The particles of the invention are used as flatting agent, anti-blocking agent, carriers for chromatography, carriers for medicaments, powder coating, gap adjustment material, toners for electrophotography, electroviscous fluid and cosmetics.

[Means for solving the problem]

[0005]

The present invention provides polyester particles characterized in that the particle comprises, as a primary component, polyester resin having ionic groups in the range of 20-2000eq./ton, the volume mean particle diameter D is in the range of 0.5-100 micrometers, having one or more independent holes filled with a gas or a liquid inside the particle and the void content of the particle is in the range of 1 - 99vol%.

[0008]

The primary component of the particles of the invention is polyester resin. The ratio of polyester resin to the total resin components should be equal to or more than 50 wt%, preferably 80wt%, more preferably 90, still more preferably 95wt% and especially 95wt%. The polyester resin of the present invention is made of polyvalent carboxylic acids and polyvalent alcohols. Examples of polyvalent carboxylic acids used for polyester resin may comprise aromatic dicarboxylic acids such as terephthalic acid, isophthalic acid, orthophthalic acid, 1, 5-naphthalene dicarboxylic acid, 2,6-naphthalene dicarboxylic acid, 9,10-anthracene dicarboxylic acid, 9, 10-anthracene dipropionic acid, diphenic acid, a sulfo terephthalic acid, 5-sulfoisophthalic acid, 4-sulfophthalic acid, 4-sulfonaphthalene-2,7-dicarboxylic acid, 5[4-sulfo phenoxy] isophthalic acids and sulfoterephthalic acid, and metal salts or ammonium salts thereof; aromaticoxy carboxylic acids sucha as p-oxybenzoic acid and p-(hydroxyethoxy) benzoic acid; aliphatic dicarboxylic acids such as succinic acid, adipic acid, azelaic acid, sebacic acid and dodecanecarboxylic acidunsaturated; aliphatic polyvalent carboxylic acids such as fumaric acid, maleic acid, itaconic acid, mesaconic acid and citraconic acid; unsaturated aromatic polyvalent carboxylic acids such as phenylene dicarylic acid; alicyclic polyvalent carboxylic acid such as hexahydrophthalic acid and tetrahydrophthalic acid and tri- or more valent carboxylic acids such as trimellitic acid, trimesic acid and pyromellitic acid.

[0012]

The glass transition temperature of the polyester resin of the invention may be equal to or more than 40°C, preferably 45°C, more preferably 50°C, still more preferably 60°C, especially 70°C. When the glass transition temperature is less than the temperature, blocking of the particles tend to occur and handling the obtained particles becomes difficult. The number average molecular weight of the polyester resin of this invention may be in the range of 1000-20000, preferably 2000-5000 and more preferably 3000-4000.

[0013]

According to the present invention, the polyester resin must contain 20-2000eq/ton of ionic groups. Examples of ionic groups may comprise anionic groups such as sulfonic, caboxylic, sulfuric, phosphoric, phosphonic and phosphinic groups and ammonium or metal salts thereof; cationic groups such as primary or tertiary amine. Preferably, metal sulfonate groups and ammonium carboxylate groups are used. The

ionic groups may be copolymerized within the polyester resin or attached to the end of the polymer chain. Examples of polyvalent carboxylic acid having a metal sulfonate moiety which can be used to copolymerize with the polyester comprise sulfoterephthalic acid, 5-sulfoisophthalic acid, 4-sulfophthalic acid, 4-sulphonaphthalene-2,7-dicarboxylic acid, 5(4-sylphophenoxy)isophthalic acid and salts thereof. In addition, metal sulfonate group may be introduced at the end of the polymer chain by using metal sulfobenzoate. The salt may be those with ammonium ions, Li, Na, K, Mg, Ca, Cu Fe, Ni, Co and Al, and K and Na salts are preferable.

[0014]

Carboxylic group can be introduced at the end of the polymer chain by adding a polyvalent carboxylic acid such as trimellitic acid during the terminal stage of the polymerization reaction. Further, the carboxylic acid may be exchanged with salt by nutralizing the same with ammonia or sodium hydroxide. The amount of the ionic group in the polyester resin is 20-2000eq/ton, preferably 20-500 eq./ton and more preferably 50-200 eq./ton. The above described properties are essential to the polyester particles of the invention.

[0015]

The detailed method for obtaining polyester resin of the invention is described below. There are two methods for preparing the perforated polyester particles of the invention, i.e. a method for obtaining the perforated particles when pulverizing; and a method for providing holes inside the particles by processing once obtained solid particles.

[0025]

The invention is further explained with the examples shown below. The present invention is not limited by the examples.

[EXAMPLES]

Preparation of polyester resin (A1)-(A3), (A6)

To the autoclave vessel equipped with the thermometer and the agitator, dimethyl telephthalate 80 parts by weight, dimethyl isophthalate 80 parts by weight, dimethyl 5-sodiumsulfo isophthalate 6 parts by weight, ethylene glycol 68 parts by weight, neopentylglycol 114 parts by weight and tetrabutoxytitanate 0.1 part by weight were loaded. The mixture was heated at 120-220°C for 120 minutes to carry out the ester exchange reaction. Then the reaction was cooled to 180°C, fumalic acid 20 parts

by weight and hydroquinone 0.1 part by weight were added thereto and reacted for 60 minutes at 200°C. After that, the reaction was heated to 220-240°C and the pressure was adjusted to 1-10 mmHg, and reacted further 60 minutes to give the copolymer polyester A1. The formulation, glass transition temperature, acid value, molecular weight, and sodium sulfonate equivalence of the obtained copolymer polyester (A1) are shown in Table 1. The formulation of the polyester resin was determined with NMR, the glass transition temperature was determined with DSC, the acid value was determined by titration, molecular weight was determined with GPC, the sodium sulfonate equivalence was calculated from the amount of S.
(A2) and (A3) shown in Table 1 were prepared by polymerizing the starting materials in the same manner as above.

[0026]
Table 1

Polyester Resin		Examples					Comp. Ex.
		A1	A2	A3	A4	A5	A6
Polyvalent Carboxylic Acids	NDC	-	40	-	-	-	-
	TPA	40	29	49	65	-	50
	IPA	40	29	48	30	-	50
	FA	18	-	-	-	-	
	MA	-	-	-	-	100	-
	SIP	2	2	3	1	-	-
	TMA	-	-	-	4	-	-
Polyvalent Alcohols	BG	50	30	40	50	-	50
	NPG	50	70	-	50	-	50
	BPP	-	-	60	-	100	-
Tg (°C)		45	79	67	59	54	58
number average Mw		3000	2800	2700	3100	2200	3000
weight -average Mw		4500	4300	3700	5300	3500	4500
acid value (mgKOH)		0.1	0.1	0.1	3.2	16.5	0.0
S equivalence (eq/ton)		110	98	125	45	0	0

Preparation of polyester resin (A4)

To the autoclave vessel quipped with the thermometer and the agitator, dimethyl telephthalate 128 parts by weight, ethylene glycol 45 parts by weight,

bisphenol A added with propylene oxide 270 parts by weight and tetrabutoxytitanate 0.1 part by weight were added. The mixture was heated at 150°C-220°C for 180 minutes to carry out the ester exchange reaction. Then the was cooled to 180°C, maleic anhydride 29 parts by weight and hydroquinone 0.1 parts by weight were added thereto and reacted for 60 minutes at 200°C. After that, the reaction was heated to 220-240, then the pressure was gradually decreased over 30 minutes to 10 mmHg and then reacted further 60 minutes. After that, the air in the vessel was exchanged with nitrogen gas and the pressure was adjusted to the ambient pressure. Trimellitic acid unhydrous 8 parts by weight was added thereto and reacted further 60 minutes at 200°C to give polyester resin (A5).

Preparation of polyester resin (A5)

To the autoclave vessel equipped with the thermometer and the agitator, bisphenol A added with propylene oxide 700 parts by weight, maleic anhydride 196 parts by weight and hydroquinone 0.1 parts by weight were added. Nitrogen gas was introduced to the reaction vessel to keep the inert atmosphere. Dibutyltin oxide 0.05 part by weight was added to the reaction and reacted at 200°C to give the polyester resin (A5) shown in Table 1.

[0027]

In the table 1, NDC represents 1,5-naphthalene dicarboxylic acid, TPA represents telephthalic acid, IPA represents isophthalic acid, SIP represents 5-sodium sulphophthalate, FA represents fumaric acid, MA represents maleic acid, TMA represents trimellitic acid, EG represents ethylene glycol, NPG represents neopentyl glycol, BPP represents bisphenol A added with propylene oxide (average molecular weight 350) and Tg represents glass-transition temperature.